



Application of lithiated Nafion ionomer film as functional separator for lithium sulfur cells

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HIGHLIGHTS

- We first applied lithiated Nafion ionomer film for Li–S cell as the separator.
- Polysulfide anions couldn't transport through the ionomer film, while Li-ion could.
- Li–S cell with the ionomer electrolyte shows an improvement in cycle performance.
- The results may offer an alternate idea to improve the performance of Li–S cell.

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ABSTRACT

Lithiated Nafion ionomer film is applied as functional separator for Li–S cells. The ionomer electrolyte is composed of the lithiated Nafion ionomer film and liquid electrolyte. The Li-ion conductivity of the ionomer electrolyte is $2.1 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. The Li-ion transference number and the elemental sulfur permeability of the ionomer electrolyte shows the polysulfide anions can transport through the ionomer film hardly. The CV result reveals the ionomer electrolyte is electrochemically stable and workable for lithium and sulfur electrodes. The initial discharge capacities of the Li–S cells with ionomer film and with liquid electrolyte are nearly the same. However, the discharge capacity of the Li–S cell with the ionomer film at the 50th cycle is found to be 815 mAh g^{-1} , and the coulombic efficiencies are above 97% along with cycles, showing an improvement in cycle performance as well as in coulombic efficiency, compared with the Li–S cell with liquid electrolyte of which the discharge capacity is 552 mAh g^{-1} at the 50th cycles, and the coulombic efficiencies are lower than 97% along with cycles.

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1. Introduction

It was reported that the realization of Lithium sulfur (Li–S) cell had a number of difficult problems to overcome, such as sulfur utilization, cycle life, and rate capability, which are mainly caused by the soluble intermediate lithium polysulfide (Li_2S_n , $3 \leq n \leq 8$) and the insoluble, highly insulative end productions (Li_2S_2 and/or Li_2S) [1–4]. During the discharge process, the lithium polysulfide can dissolve in the electrolyte and transport through the separator to the Li electrode, where they can react directly to create the solid products (Li_2S_2 and/or Li_2S), which extensively precipitate on the surface of anode electrode, contributing to the loss of active mass and the corrosion of electrodes [5]. And during the charge process, the shuttle phenomenon, which is also caused by the transportation of polysulfide anions, causes the decrease of coulombic efficiency [6].

Many efforts had been made to immobilize the polysulfide anions in Li–S cell. Different kinds of carbon with special structure were used in cathode [7–9]. The carbons act not only as the electrically conductive components but also the framework and the sorption properties to inhibit the transportation of lithium polysulfide. Attention has also been paid to Li surface modification to slow down or completely prevent further interaction of metal lithium with polysulfide anions, by optimizing the electrolyte composition to form an in situ protective layer [10,11], or depositing protective films on the lithium surface in advance [12].

Nafion ionomer film, a copolymer of tetrafluoroethylene and perfluoro vinyl ether, e.g. $-(\text{CF}_2\text{CF}_2)_m-(\text{CF}_2\text{CF}(\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}))_n$, which is widely used in the proton exchange membrane fuel cells and chlorine–caustic soda industry, is well-known with its excellent stability, high cationic conductivity and unity transference number. When turned to Li^+ form, it has the potential to transfer Li^+ and prevent the polysulfide anions from transporting through, due to its special structure. Doyle and Sachan studied the ionic conductivity and swelling behavior of lithiated Nafion ionomers in a wide range of nonaqueous solvents

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respectively [13–15]. Liang studied LiCoO_2 cell using lithiated Nafion film swollen with propylene carbonate/ethylene carbonate mixture as electrolyte, indicating that the ionomer electrolyte is usable in the Li-ion cell [16].

In this work, we use the lithiated Nafion ionomer film with liquid electrolyte as a polymer electrolyte in Li–S cell, to inhibit the transportation of polysulfide anions, which could improve the cycle performance and the coulombic efficiency of Li–S cell. This paper reports our preliminary results on the Li–S cell by using the ionomer electrolyte.

2. Experimental

2.1. Preparation of lithiated Nafion ionomer electrolyte

Nafion-212 ionomer film was purchased from Dupont Company in H^+ form. The lithium-ion exchange procedure was carried out in a solution of 1.0 M LiOH in H_2O : ethanol (1:1 by weight) mixture at 80°C for 12 h under vigorous stirring [17]. The resulting lithiated Nafion ionomer film was then rinsed in boiling deionized water to remove the remaining salt and organic solvent. After vacuum drying at 120°C overnight, it was transferred into an argon-filled glove box.

The ionomer electrolyte was composed of the lithiated Nafion ionomer film and liquid electrolyte. A solution of 1.0 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in dioxolane (DOL) and dimethoxyethane (DME) (1:2 by weight) mixture (Ferro Inc.) was used as liquid electrolyte. For comparison, the liquid electrolyte was also used in Li–S cell with Celgard 2400, which has not any interaction with ions in liquid electrolyte, as the separator.

2.2. Preparation of cathode

The cathode was fabricated with sulfur, Super P carbon and PVdF binder in weight ratio of 70:20:10. The cathode slurry was prepared by ball milling and then casted onto an Al foil by using a doctor blade. After vacuum drying 12 h at 70°C , the cathode was transferred into the glove box.

2.3. Characterization

The FT-IR absorption spectra were recorded on Nicolet 5700 Fourier transform IR spectrometer over the range of $1800\text{--}800\text{ cm}^{-1}$. The resolution was set to 2 cm^{-1} .

Li-ion conductivity of the ionomer electrolyte was determined by using electrochemical impedance spectroscopy (EIS), on a cell assembled by sandwiching the ionomer electrolyte between two stainless-steels.

Li-ion transference number of the ionomer electrolyte was determined by using the steady-state current method [18], on a cell assembled by sandwiching the ionomer electrolyte between two Li foils. The method consists of initial measurement of the lithium interfacial resistance (R_0), then application of a small voltage (ΔV , 10 mV) until a steady current (I_{ss}) is obtained, and final measurement of the interfacial resistance (R_f). Li-ion transference number (t_{Li^+}) is calculated using the equation $t_{\text{Li}^+} = (I_{ss}(\Delta V - I_0 R_0)) / (I_0(\Delta V - I_{ss} R_f))$, where I_0 is the initial current and is calculated from the voltage and the initial overall cell resistance by $I_0 = \Delta V / (R_e + R_0)$, where R_e is the electrolyte resistance.

The cyclic voltammogram and the charge–discharge performance were measured on a coin cell, which was assembled by stacking in turn the sulfur cathode, the ionomer film or Celgard 2400 with liquid electrolyte, and Li foil. The sweep rate of cyclic voltammogram is 0.5 mV s^{-1} . The charge–discharge performance

was evaluated by cycling the cells between 2.5 and 1.5 V at current density of 0.3 mA cm^{-2} .

The elemental S permeability was obtained on a diffusion cell. The diffusion cell consists of two PTFE reservoirs, one for cathode and the other for anode, and a circularly symmetrical transport channel with a separator clamped between them. The separator is the ionomer film or Celgard 2400. To measure the elemental S permeability, an elemental S-free Li salt, LiNO_3 , was used in the DOL and DME mixture. Liquid samples of a constant volume of $100\text{ }\mu\text{l}$ were taken at prescribed time intervals in the anode reservoir during a discharge process, and then the concentrations of the elemental S were determined by inductively coupled plasma–anodic emission spectrometer (ICP–AES). The discharge process lasted 96 h at current density 0.1 mA cm^{-1} .

All the cells were assembled in the argon-filling glove box. The Li-ion conductivity, cyclic voltammogram and Li-ion transferences number were investigated with VersaSTAT (Princeton Applied Research). The charge–discharge performance was investigated with Land CT2001A test system.

The morphologies of the Li anode surface before discharge, and after 50th fully discharged in Li–S cell with different electrolyte were investigated by scanning electron microscopy (SEM, S4800, Hitachi).

3. Results and discussion

The FT-IR spectra can be used to verify the conversion of the ionomer film from the H^+ form to the Li^+ form. A thorough

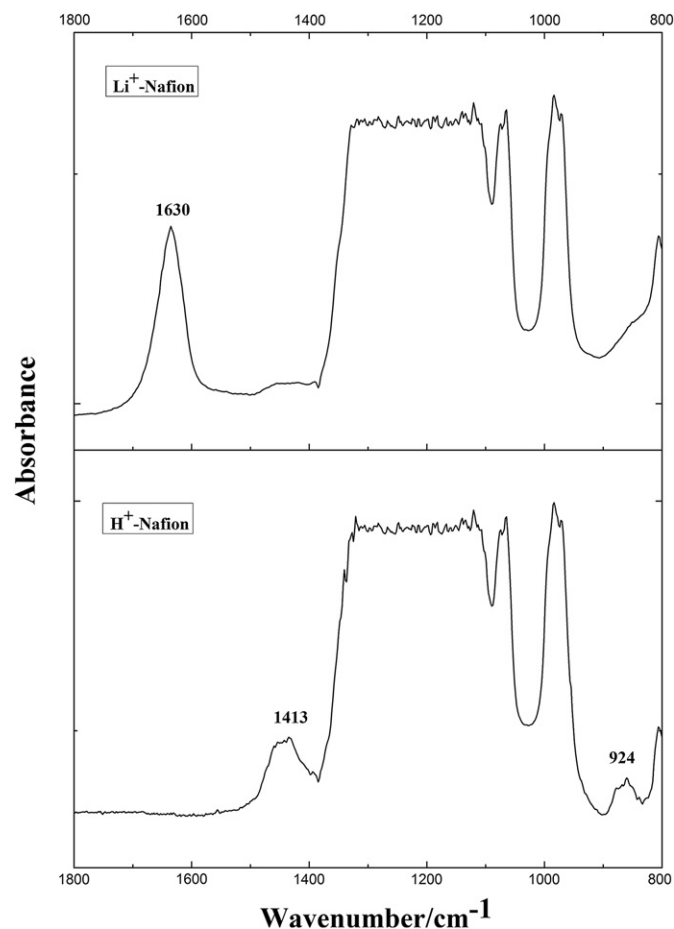


Fig. 1. FT-IR spectra of the Nafion ionomer films in different forms over the range of $1800\text{--}800\text{ cm}^{-1}$.

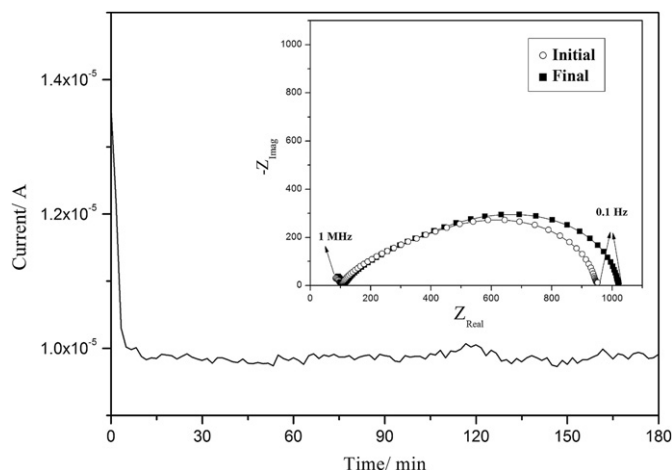


Fig. 2. Measurement taken for Li-ion transference number determination by the steady-state current method. Applied voltage was 10 mV. Parameters obtained for t_{Li^+} calculation: $I_{\text{ss}} = 9.88 \mu\text{A}$, $R_e = 101.5 \Omega$, $R_0 = 849.5 \Omega$, $R_f = 907.8 \Omega$.

analysis of the IR behavior of Nafion ionomer in different cationic forms has been done [19]. FT-IR scans of the H^+ form ionomer film and Li^+ form ionomer films are shown in Fig. 1. The vibrational modes of the film cannot be observed between 1400 and 1100 cm^{-1} , due to the thickness of the film. The conversion from the H^+ form to the Li^+ form was verified by the disappearance of the 924 and 1413 cm^{-1} bands, which are assigned to S–OH and S=O stretching modes of the undissociated $-\text{SO}_3\text{H}$ groups in H^+ form film, and the appearance of the 1630 cm^{-1} band in Li^+ form film [14].

The outcomes of using steady-state current method to measure t_{Li^+} of ionomer electrolyte are shown in Fig. 2. Parameters obtained for t_{Li^+} calculation were: $I_{\text{ss}} = 9.88 \mu\text{A}$, $R_e = 101.5 \Omega$, $R_0 = 849.5 \Omega$, $R_f = 907.8 \Omega$. It is calculated that t_{Li^+} was 0.986, with which a near unity could be expected, indicating that only Li^+ could transport through the ionomer electrolyte, while anions couldn't.

Further unequivocal proof that the polysulfide anions couldn't transport through the ionomer electrolyte arises from the experiment of the elemental S permeability. The concentration of elemental S in the anode reservoirs using ionomer film and Celgard 2400 as separator respectively at different times is shown in Fig. 3. The decrease of elemental S concentration using Celgard 2400 after 48 h may be due to the forming of Li_2S_2 and Li_2S which precipitate

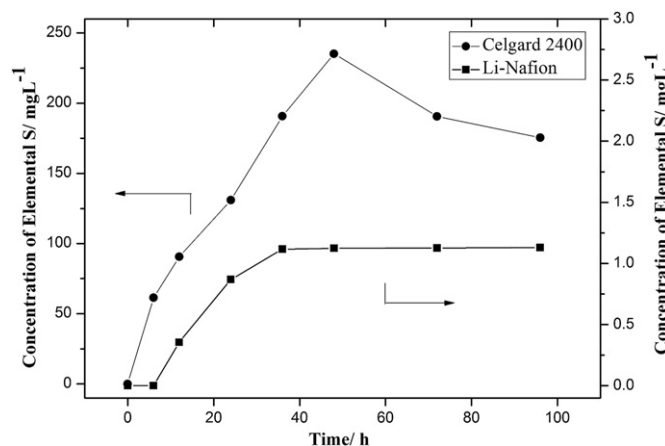


Fig. 3. Concentration of elemental S in the anode reservoirs using ionomer film and Celgard 2400 respectively as separator at different times.

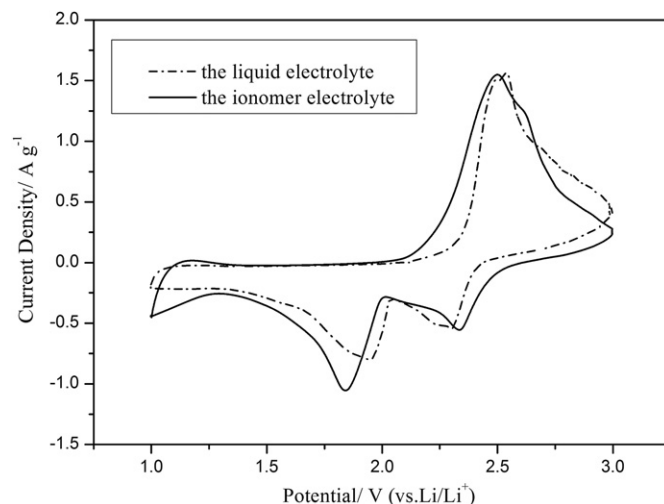


Fig. 4. CV of the Li-S cells with liquid electrolyte and the ionomer electrolyte at the sweep rate of 0.5 mV s^{-1} .

on the surface of Li metal. As illustrated in Fig. 3, using ionomer film showed a dramatically lower elemental S permeability than that observed using Celgard 2400 in the anode reservoir, indicating that polysulfide anions hardly transport through the ionomer film.

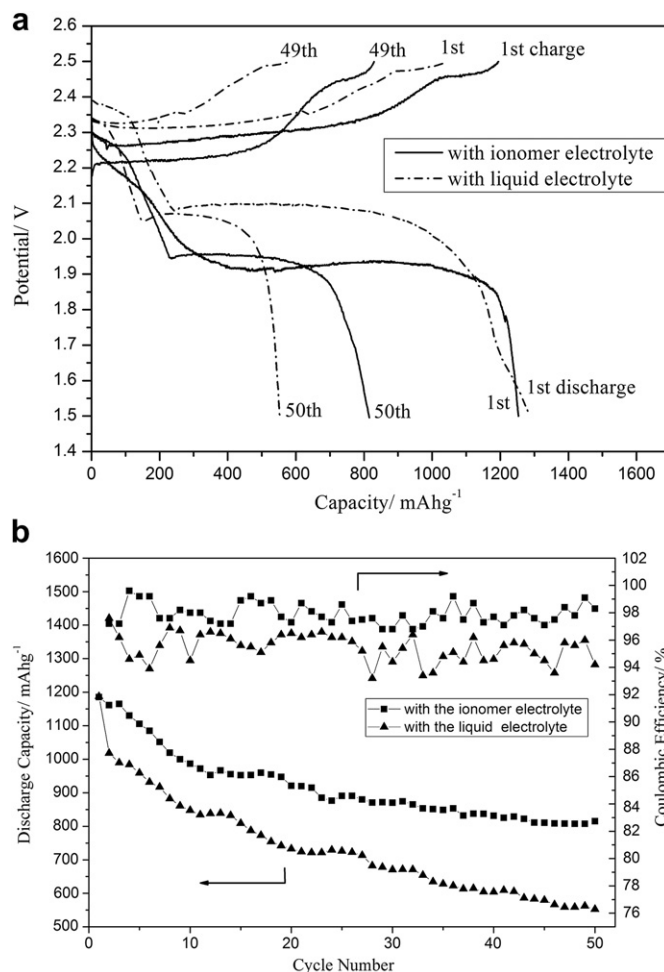


Fig. 5. Electrochemical tests of Li-S cells with the ionomer electrolyte and liquid electrolyte in the range of 2.5–1.5 V at current density of 0.3 mA cm^{-2} (a): The discharge/charge curve of at the initial cycle and the end cycle. (b): The cycle performance and the coulombic efficiencies.

Although the polysulfide anions transport in the electrolyte is mainly controlled by Fickian diffusion, it is believed that the special structure of the ionomer film is most likely to cause some anomalies to polysulfide anions transport mechanism. Compared with Celgard 2400, in which the polysulfide anions could transport freely, the ionomer film has $-\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2-\text{CF}_2\text{SO}_3\text{Li}$ pendent side chains, which are immobile in the electrolyte. When Li^+ dissociated from the side chains, the $-\text{SO}_3^-$ groups formed an electric force field, offering the Li^+ transference and preventing the polysulfide anions from transporting through. And the channels and clusters structure of the ionomer film serves as a transporting barrier as well [20].

The cyclic voltammogram of Li–S cells with the ionomer electrolyte and liquid electrolyte is shown in Fig. 4. The CV of the Li–S cell with the ionomer electrolyte exhibited typical characteristic oxidation and reduction peaks of elemental sulfur, and no additional peaks are found, indicating that the electrochemical stability of the ionomer electrolyte is sufficient for use in Li–S cell. Although the ionomer electrolyte has low Li^+ conductivity ($2.1 \times 10^{-5} \text{ S cm}^{-1}$) measured by EIS, the ionomer electrolyte is suitable for Li–S cell to improve the cycle performance and coulombic efficiency.

The oxidation peak at 2.50 V is attributed to the conversion of lithium polysulfide into sulfur and lithium. The two reduction peaks are corresponding to the two steps reduction of sulfur: the first at 2.35 V represents reduction of solid sulfur to soluble intermediate lithium polysulfide, and the second represents further reduction of lithium polysulfide to solid lithium sulfides [6]. However, a distinction is recognized that the reduction peak at about 2.0 V in the cell with liquid electrolyte is shifted to 1.85 V in the cell with the ionomer electrolyte, which is caused by the concentration polarization of the polysulfide anions. The intermediate polysulfide anions trend to transport to the anode under electric field and concentration driving. When they could not transport through the ionomer membrane, the intermediate

polysulfide anions accumulates on the membrane side, and causes the reduction potential difference.

The initial and the end charge–discharge curve of Li–S cells with the two electrolytes shows two voltage plateaus in Fig. 5(a), corresponding to reduction peak in the CV curve. Although the two voltage plateaus of the Li–S cell with the ionomer electrolyte decreased, the initial capacity of the cell is nearly the same to the cell with liquid electrolyte at the cut-off voltage. The initial discharge capacities of Li–S cells with the ionomer electrolyte and the liquid electrolyte are about 1185 mAh g^{-1} and 1187 mAh g^{-1} , respectively. However, the discharge capacities and the coulombic efficiencies of Li–S cell with the ionomer electrolyte are higher than the ones of Li–S cell with the liquid electrolyte at the following cycles, as shown in Fig. 5(b). The discharge capacity of the Li–S cell with the ionomer film at the 50th cycle is found to be 815 mAh g^{-1} , retaining 69% of the initial discharge capacity, and the coulombic efficiencies are above 97% along with the cycles, showing an improvement in cycle performance as well as in coulombic efficiency, compared with the Li–S cell with liquid electrolyte, which has the discharge capacity of 552 mAh g^{-1} at the 50th cycles, and the coulombic efficiencies lower than 97% along with the cycles.

SEM of images of the Li surface of the cells with different electrolyte after 50th fully discharges are shown in Fig. 6, compared with the Li surface before discharge. The Li surface before discharge is compact and smooth, as shown in Fig. 6(a). After 50th fully discharge, the Li surface in the cell with both the ionomer electrolyte and the liquid electrolyte are shown in Fig. 6(b) and Fig. 6(c), respectively. Greater cracks and more precipitations were found on the Li surface in the cell with liquid electrolyte. The greater cracks mean more corrosion occurs. The precipitations are made of Li_2S_2 and Li_2S , which are highly insulative. When they precipitate on the surface of Li anode, they would not take part in electrochemical oxidation during the next charge processes.

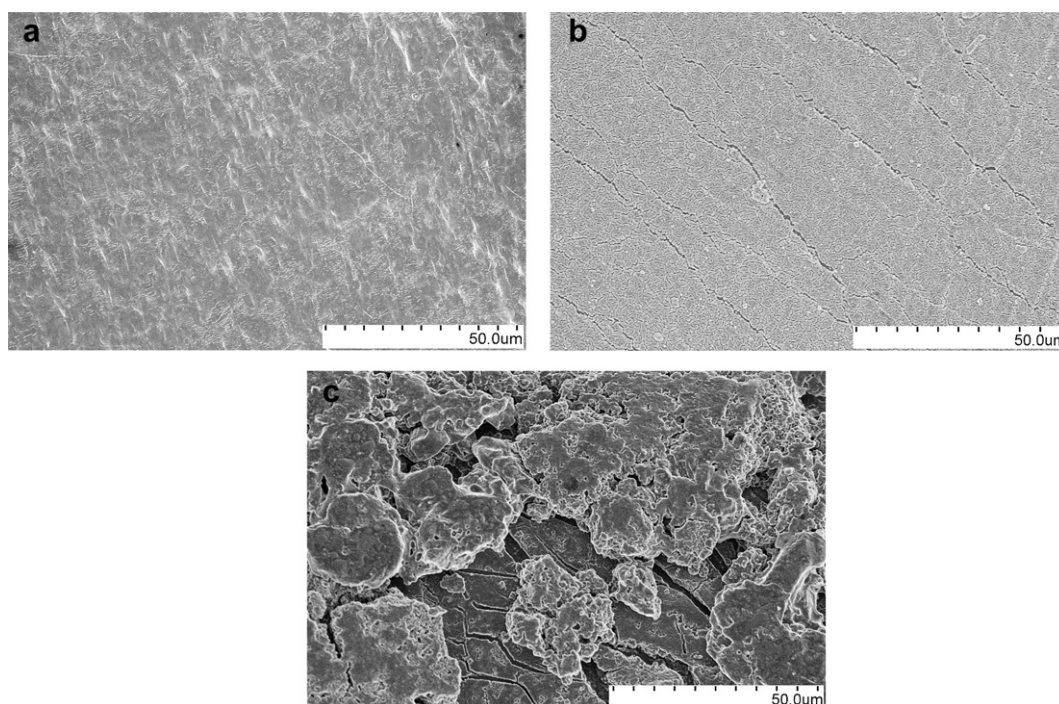


Fig. 6. SEM of images of the surface of Li anode: (a) before discharge, (b) Li–S cell with ionomer electrolyte after 50th discharged, and (c) Li–S cell with liquid electrolyte after 50th discharged.

The SEM images explain the reason of the cycle performance improvement. The ionomer electrolyte prevents the polysulfide anions from transporting through the electrolyte. Once the polysulfide anions couldn't react with metal Li, the problem occurring in Li–S cell with liquid electrolyte, such as loss of active mass, Li surface corrosion and shuttle phenomenon would less occur. Unfortunately, the discharge capacities of the Li–S cell with the ionomer electrolyte are still fading along with the cycles. It may be caused by the forming of passivation layer on the cathode surface [21]. Optimizing the cathode structure based on the basis of ionomer electrolyte may achieve better outcomes.

4. Conclusion

In this work, we used the lithiated Nafion ionomer film as polymer electrolyte for Li–S cell. The experiment of t_{Li^+} and elemental S permeability of the electrolyte showed that the polysulfide anions could hardly transport through the electrolyte. It is found from CV evidence that this electrolyte is chemically and electrochemically stable toward lithium and sulfur.

Although concentration polarization was found in the cell with ionomer electrolyte, the initial capacity was almost the same as the cell with liquid electrolyte, and the capacities and the coulombic efficiencies were higher at the following cycles than the cell with liquid electrolyte. The improvements of cycle performance and coulombic efficiency were due to the untransportable polysulfide anions through the ionomer film, which helped to decrease the loss of active mass and the corrosion of Li electrode, and inhibit the

shuttle phenomenon. The strategy of using the ionomer electrolyte can be potentially generalized for improving the performance of Li–S cells.

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